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Flammability and volatility attributes of binary mixtures of some practical multi-component fuels

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HIGHLIGHTS

- Measured the flash point and volatility of binary multi-component fuel mixtures.
- Light naphtha blended at >20% vol. with diesel has a flash point below −40 °C.
- n-Butane can be used with diesel/gasoline mixtures to meet flammability needs.
- Changing ambient temperature does not significantly alter the flammability limits.
- An equation has been developed to predict flash point from other fuel properties.

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ABSTRACT

Gasoline compression ignition (GCI) engines could be more efficient than most advanced SI engines while running on lower octane fuel. GCI engines may utilize a mixture of different fuels and fuel components such as gasoline and diesel or diesel and naphtha. The risks and hazards associated with such mixtures must be studied to ensure safe fuel storage, shipping and dispensing. In this work, flash point and vapor pressure measurements of different binary multi-component hydrocarbon mixtures are presented along with calculated lower and upper flammability limits. An equation has been developed to correlate flash point with other fuel properties. The flash point of a mixture approaches the flash point of the more volatile component, falling rapidly in some cases, as the more volatile component concentration increases. Vapor pressure is inversely related to flash point for a given mixture. Diesel/light straight run naphtha mixtures and diesel/gasoline mixtures exhibit similar flash point versus vapor pressure trends. Flammability limits were calculated using Le Chatelier's Mixing Rule and modified Burgess–Wheeler Law. Hydrocarbon mixtures have similar lower and upper flammability limits over a range of temperatures. The vapor pressure of fuels and fuel blends has been used to determine the safe operating region as a function of blending formula and temperature. This work demonstrates that normal butane can be used to formulate blends of gasoline and naphtha with diesel, which are safe to handle and meet seasonal vapor pressure requirements.

1. Introducterion

Nearly all transport energy is derived from liquid fuels made from crude oil, and transport fuels account for 60% of the total oil consumption worldwide [1]. The demand for transport fuels is growing but this growth is heavily skewed toward commercial transport and hence toward diesel and jet fuel (as opposed to gasoline) [1–3]. This demand shift, combined with a push to higher octane requirements for spark ignition engines, is likely to result in a surplus of low octane components in the gasoline boiling range.

One possible solution is to develop engine/fuel systems that can utilize such light and low octane components of gasoline in the most beneficial manner. Examples of these new engine/fuel systems are gasoline compression ignition (GCI) [2] and octane on demand (OOD) [4]. GCI engines can be as efficient as current diesel engines, while operating on low cost, low octane gasolines (such as naphtha). In the short term, such new combustion systems may have to run on existing market fuels and available fuel components. This can be accomplished by blending diesel and gasoline to achieve the lower octane number fuel needed by GCI engines

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[2,5]. Eventually, GCI engines will be well positioned if they are able to consume surplus low octane gasoline blendstocks like naphtha. It is also possible that mixtures of diesel fuel and naphtha would provide the optimum fuel quality needed by GCI, while providing lower cost and carbon emissions relative to diesel fuel. The hazards and risks associated with such blends need to be studied.

The headspace of a fuel tank contains a mixture of fuel vapors and air. Vapor pressure is an important property of automotive and aviation gasoline [6]. It is used to set a standard at which the fuel would be safe for handling. Vapor pressure is also important for cold-start and warm-up in spark ignition engines [7]. Low vapor pressure fuels result in starting difficulties, sluggish warm-up and acceleration reduction [8]. While high vapor pressure fuel could cause vapor lock, resulting in decreased fuel flow to the engine. Vapor pressure and ambient pressure will determine the gas composition at the vapor liquid interface according to Henry's law. Gasoline standards limit the vapor pressure depending on the country, region, and season, e.g., within a range of 48.2–103 kPa in the U.S. [7].

There are different standards to measure vapor pressure. These include dry vapor pressure equivalent (DVPE), ASTM test method D5191 [9], and Reid vapor pressure (RVP), ASTM test method D323 [10]. Both methods have been designed to determine the vapor pressure of gasoline and other volatile crude products. DVPE uses an automated vapor pressure instrument to detect the total vapor pressure applied in vacuum [9]. Moreover, DVPE has the ability to detect vapor pressure of a fuel whether it contains oxygenates or not. In contrast, RVP is limited to fuels that do not contain oxygenates. DVPE depends on a statistical equation that applies a correction factor to the measured total vapor pressure [9]. The vapor pressure of mixtures can also be estimated using Raoult's Law, which states that the vapor pressure of an ideal mixture is equal to the vapor pressure of each component within that mixture times its mole fraction [11].

Petroleum-based fuels contain hundreds of different hydrocarbons, each with a different boiling point [7]. Therefore, each fuel will have a unique boiling range (rather than a boiling point as with a single component). The relationship between temperature and the amount of fuel evaporated is known as the distillation curve [1]. There are several ASTM test methods that can be used to produce such distillation curves – D86 [12], D7345 [13] and D2887 [14]. All these test methods can be used to determine the range at which the petroleum products will boil, although they cover different boiling ranges. In this study, ASTM test method D2887 was used to determine the distillation curve for the fuels of interest.

Most industrial processes consider flammability limits to be a major safety concern [15]. Many hydrocarbons are volatile at normal conditions, thus knowledge of flammability limits is needed to prevent explosive hazards. At a given temperature, the lower flammability limit (LFL) and the upper flammability limit (UFL) are, respectively, the lowest and highest concentration of a hydrocarbon (volume %) in air at which a flame can be initiated by an ignition source [16]. In other words, concentrations below the LFL are too lean, whereas the ones above the UFL are too rich, to support a propagating flame. Fire protection engineers therefore utilize flammability limits when assessing the potential risk posed by a flammable substance [15].

There are many methods to obtain reliable flammability limits, to handle flammable gasses safely [15]. These flammability limits can be measured. For example, an ASTM test method E681 can identify flammability limits through the visual detection of a propagating flame initiated by an electric ignition source [17]. This test is costly. Therefore, correlations have been proposed to predict them in the absence of experimental measurements. Shimy demonstrated that flammability limits of all hydrocarbons with multiple molecular structures depend mainly upon the required energy for two carbon atoms to be disengaged [18]. In 1891, Le Chatelier demonstrated an empirical equation to predict flammability limits of fuel–air mixtures in the gas phase from fundamental properties [19]. Zhao established a comparison between experimental flammability limits and the predicted ones using Le Chatelier's Mixing Rule [15]. The probability of ignition varies from 0% to 100% depending on the vapor concentration at a given temperature [16]. At a certain point slightly below the calculated upper flammability limit, the mixture would have a 100% probability in terms of producing a sustainable, propagating flame [16]. Various other correlations have established relationships between flammability limit and other parameters, such as molecular weight and molecular structure [20,21].

If the mixture is between the upper and lower flammability thresholds, an accidental spark could create an explosion. One measure used to quantify the risk of explosion is the flash point, which is the lowest temperature at which the fuel can vaporize to form an ignitable mixture in air [22]. In other words, it is approximately the minimum temperature at which the vapor pressure of the fuel exceeds the lower flammability threshold. Lower flammable limit, compared to flash point, requires lower concentration of flammable vapors [20]. Commercial gasoline in the market has a flash point less than −40 °C. At ambient temperatures the air/fuel vapor mixture is too rich to ignite because the vapor pressure at these conditions exceeds the upper flammability threshold. Diesel fuel has a flash point of around 60 °C and the air/fuel mixture in the head space is too lean to ignite at normal ambient temperatures. Blending light fuels like naphtha or gasoline with diesel changes the vapor pressure characteristics and therefore the flash-point – potentially creating a hazardous situation.

Flash point can be measured in a standardized test such as IP 170 [22]. Several studies have also developed correlations to predict flash points of binary hydrocarbon mixtures. Such methods are unsuitable for mixtures that have a wide boiling range such as gasoline/naphtha and diesel. Establishing a sound understanding of the flash point would assist in achieving safer fuel formulations.

There are two procedures used to measure flash point temperature. These are the closed cup and open cup methods. Since vapors are vulnerable to escape in the open cup method compared with the closed cup, the closed cup flash point temperature is lower than the open cup [23]. Flash point temperatures can be determined from the literature for pure liquids, but not for mixtures [23].

Prediction models have been established to approximate the flash point temperatures for both pure components and mixtures. Wickey and Chittenden introduced an index based model to calculate the closed cup flash point [24]. Catoire and Paulmier also developed an empirical model to predict the flash point temperature assuming a non-ideal solution [25]. Rowley proposed a structural group contribution model based on the well-known Clausius–Clapeyron equation (which relates the vapor pressure dependence on temperature of a pure component to its heat of vaporization) [26]. Shimy correlated the flash point of any compound of paraffinic hydrocarbons, paraffinic isomers, olefins, benzene series, acetylene and alcohols with the ignition temperature of that compound [18].

These predictive equations for flammability limits are limited to 25 °C and atmospheric pressure. An understanding of flammability limit changes with respect to temperature must also be established to address hazards associated with fuel storage and distribution. The modified Burgess–Wheeler Law with Spakowski's assumption can relate the flammability limit with temperature change [27,28]. Flash point measurements for blends of a Saudi gasoline and a Saudi diesel fuel were reported in [5].